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Materials Processing of Diamond:  
Etching, Doping by Ion Implantation and Contact Formation

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## I. OVERVIEW

We are studying implantation doping, etching, contact formation, and regrowth of natural diamond, for future applications to the fabrication of devices from thin film CVD diamond. In addition, we are characterizing thin film diamonds of other ONR contractors, using ion beam methods.

### 1. Doping

In diamond, implantation doping is difficult because the high annealing temperature necessary to remove damage and to obtain efficient dopant activation often causes graphitization. We have used an innovative co-implantation of C plus the desired dopant at 77 K, followed by rapid thermal annealing (RTA) or furnace annealing, to overcome this problem.

### 2. Etching

The removal of surface layers of diamond by polishing or chemical etching is hampered by its extreme hardness and chemical inertness. We have demonstrated that reactive ion etching with O is an effective method of removing controlled amounts of diamond.

### 3. Contact formation

We have developed a new sputtering method of forming strong metallic contacts to diamond at ambient temperatures, which may prove invaluable for microelectronics and heat sink applications.

### 4. Regrowth

Factors affecting epitaxial regrowth of damaged natural diamond are crucial for both ion beam doping and CVD growth. We have successfully regrown C-ion implanted natural diamond layers by RTA or furnace anneals.

### 5. Characterization

We have measured the H, N, and O contents of CVD diamond and ion beam deposited diamond films. We have also developed a coincidence ion scattering

method for studying impurity and dopant profiles in diamond.

## II. RESULTS

### 1. Ion implantation doping

Co-implantation of natural diamond at 77 K with C and B, followed by P A at 1100°C has been effective in producing substitutional B. The resistivity was reduced to the very low level of 100  $\Omega\text{cm}$  at 295 K, with a carrier activation energy of 0.1 eV for a sample implanted with  $2 \times 10^{15}$  C and  $3 \times 10^{14}$  B/cm<sup>2</sup>. A strong optical absorption band at 0.37 eV, corresponding to that seen for type IIb diamond, as well as unusual absorption bands near 1060 cm<sup>-1</sup> were observed.

All of these absorption bands increased in magnitude with increasing B dose. Both the low resistivity and the optical absorption bands were absent for samples implanted only with C ions. These results were reported in refs. 4, 5, 7, 10 (see Appendices 1-3).

In addition, co-implantation of C plus N or P gave encouraging results, as shown by the resistance versus temperature data of Fig. 1. Preliminary thermo-emf measurements showed that these implanted layers were n-type.

We have studied deep implants of C, B, C+B, and Cu in natural diamond, with the object of improving the epitaxial regrowth because of the constraint of relatively good diamond above the damaged layers. Excimer laser annealing as well as conventional annealing was used for these studies. In addition, we have implanted As and Li and will implant F in order to obtain n-type doping.

Outstanding results have been obtained by C+In implants at 293 K. In this case, perturbed angular correlation (PAC) results have shown that subsequent annealing at 1100°C caused 15-20% of the In atoms to reside at well defined lattice sites, probably associated with single vacancies. Such experiments could be used to measure the migration energies of both self-interstitials and vacancies in diamond, by the shrinking or growth of the In-vacancy defects.

## 2. Etching

Etching of natural diamond has been achieved using oxygen and hydrogen plasmas. Etching rates of 35 nm/min were achieved using 300 eV oxygen ions. Adding as much as 85% argon to the reaction chamber did not reduce the etch rate (ref. 6; see Appendix 4). In addition, etching was studied with gas mixtures such as  $\text{CF}_4 + \text{O}_2$  and  $\text{SF}_6 + \text{O}_2$ . So far, pure oxygen seems to give the maximum etching rate. We plan to experiment with pure  $\text{F}_2$  in the future.

## 3. Contact formation

An Ar sputtering method (patent pending) for preparing diamond surfaces was found to enhance greatly the contact strength of deposited Au films. The films were also much smoother after this treatment (Ref. 11). Current versus voltage measurements on natural semiconducting type IIb diamonds deposited with gold electrodes using the above method demonstrated ohmic type behavior (see Appendix 5).

## 4. Regrowth

The epitaxial growth of diamond, either during CVD or ion beam deposition, or after damaging by ion implantation, is important in developing diamond opto-electric devices. We have observed that good epitaxial regrowth of C-implanted natural diamond is achieved by either RTA at  $1100^\circ\text{C}$  or by furnace vacuum annealing at  $700\text{--}900^\circ\text{C}$  (refs. 8,9) when the diamond structure was not completely randomized. If the diamond was randomized (as observed by ion channeling), good epitaxial regrowth was achieved by furnace annealing, but a thin graphite layer was formed on the surface. This effect indicated that a constraining diamond layer over the damaged layer prevented graphite formation (see Appendix 6).

We plan to continue studies of regrowth, with emphasis on the influence of (1) implantation depth and (2) added impurities such as F and H.

## 5. Characterization

Elastic recoil detection was used to measure the H content of CVD thin

films from RTI as described in the previous annual report. Nuclear reaction analysis was used to measure O and N contents of ion deposited samples from the University of Houston. Nuclear reaction analysis of  $^{14}\text{N}$  and  $^{16}\text{O}$  can be achieved using deuteron ( $^2\text{H}^+$ ) or  $^3\text{H}^+$  ion beams (refs. 14,15). The cross sections for the reactions  $^{14}\text{N}(\text{d},\text{p})^{15}\text{N}$ ,  $^{16}\text{O}(\text{d},\text{p})^{17}\text{O}$  and  $^{16}\text{O}(^3\text{He}, \alpha)^{15}\text{O}$  are a few mb  $\text{sr}^{-1}$ , giving a sensitivity of about  $10^{14}$  atoms  $\text{cm}^{-2}$  or one-tenth of a monolayer, depending somewhat on the substrate. The disadvantages of the deuteron analysis are that backgrounds arise from reactions both with the substrate and with accumulated deuterium, and that neutron radiation arises from deuteron interactions. The use of the  $^3\text{He}$  avoids these problems, and is thus attractive for oxygen analysis (Ref. 15). A concentration-depth profile can also be obtained by standard energy analysis of the emitted particles. We found that the ion deposited diamond-like films contained less than 1 % oxygen.

We have also done preliminary ion channeling measurements of the quality of homoepitaxial diamond films from RTI. By the channeling method, the perfection of the diamond film can be determined. Specifically, the defect structure, mosaic spread, and lattice strain can be measured. These preliminary measurements were reported at the Diamond Technology Initiative Symposium in July 1989.

In addition, we have measured the quality of Ni crystals and Cu-Ni strained layer superlattices prepared at RTI for heteroepitaxial growth studies.

We have developed a new ion beam coincidence method to measure concentration-depth profiles of impurities in thin films of diamond (ref. 16). The idea behind the method is that measurement of the energies of both the scattered ion and the recoiled impurity atom in coincidence gives the same depth information as that obtained by the conventional measurement of the energy and scattering angle of one particle. Thus detectors can be positioned very close to the sample, so that the counting efficiency can be greatly increased. This method has been used for thin Si crystals, and will be tried for diamond films soon.

### III. CONCLUSIONS

Our implantation doping methods have great promise to achieve p- and n-type doping in diamond. Results with B and preliminary data for N and P are encouraging. Consequently, viable device fabrication is possible. Our plasma etching results (as well as those of Geis) demonstrate the feasibility of diamond lithography. Our sputtering method to improve contact adhesion will facilitate many diamond applications.

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#### APPENDICES

I - III: Refs. 4,5,7

IV: Ref. 6

V: Ref. 11

VI: Ref. 8

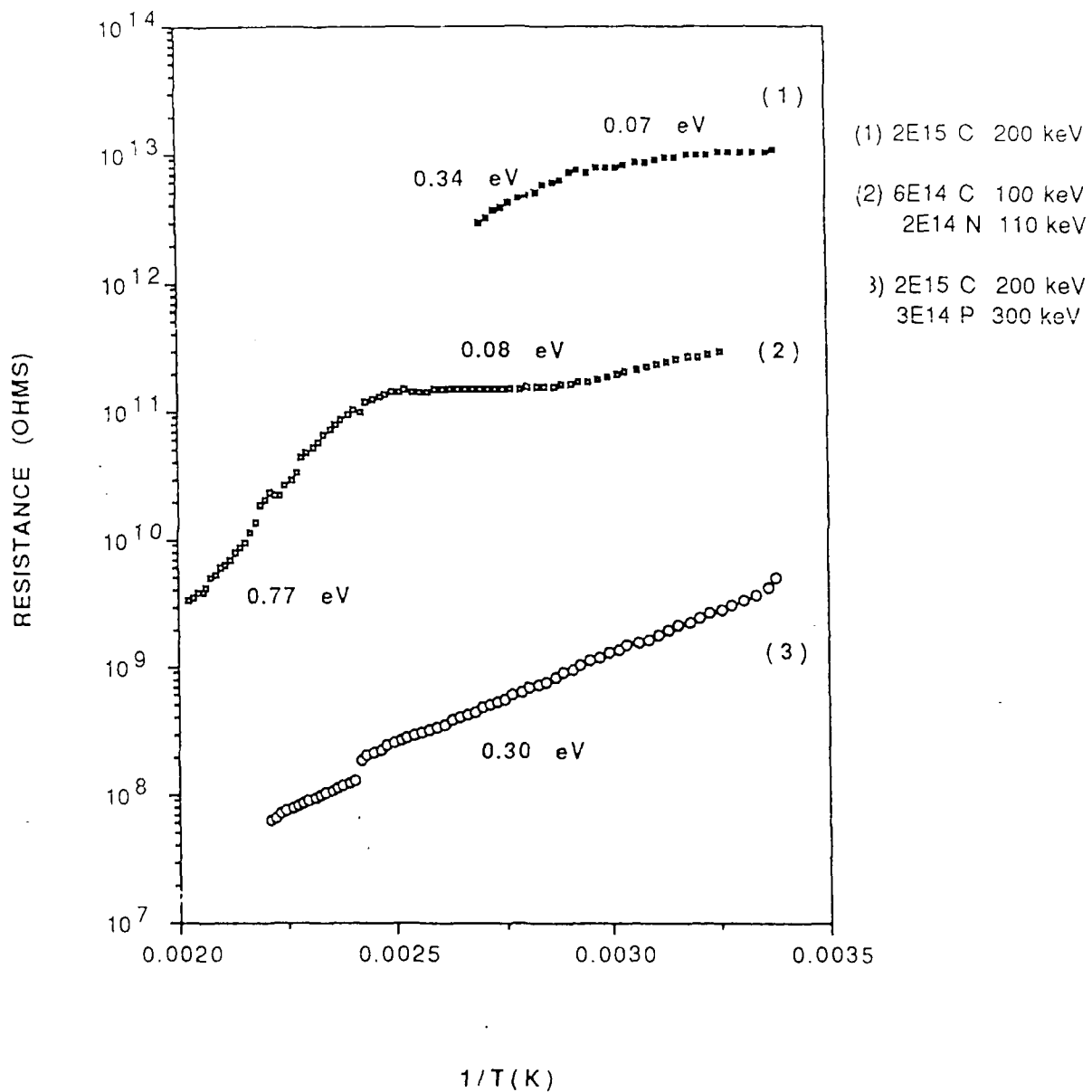


FIG. 1. Electrical resistance versus reciprocal temperature for diamond implanted with C alone and with C plus N or P, followed by RTA at 1100 C.



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# Appendix I

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## ION IMPLANTATION OF BORON IN DIAMOND

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### ABSTRACT

It has been a challenge to inject dopant atoms onto diamond lattice sites by ion implantation, because of the complications of ion damage and defect clustering during annealing. We re-investigated this topic by implanting boron ions into an insulating natural diamond (type II-A) which was pre-damaged by carbon ion implantation. Both of the implantations were performed at liquid nitrogen temperature. The amount of pre-damage was adjusted to produce enough vacancies and interstitials in diamond to promote boron substitutionality during subsequent annealing. Samples were characterized by optical absorption and electrical measurements. It was found that optical absorption of the implanted samples strongly depends on the post implant annealing sequence. The activation energies obtained from electrical measurements match very closely to those due to boron atoms in natural p-type diamonds. Photoconductivity measurements showed that the fraction of remaining electrically active radiation defects in the implanted and annealed samples depends on the relative fluences of boron and carbon.

### INTRODUCTION

Diamond based semiconductor devices may turn out to be of significant importance thanks to the unique physical and electronic properties of diamond. Few such devices have been realized till now because of difficulties in doping. Standard doping techniques such as diffusion or introduction of impurities during crystal growth are not applicable because of the high temperatures required for the former and the absence of any reliable technique for the latter. Therefore, the most promising way to dope diamond in a controlled manner is by means of ion implantation. So far, this method has yielded only limited success [1,2] because it requires finding annealing conditions which will drive the implants into electrically active sites and restore the diamond crystal structure, a task which is complicated by the tendency of the damaged diamond to turn into graphite [3,4]. When the ion dose is low enough to prevent graphitization, very few of the dopant atoms end up in electrically active sites [1,4].

It has been shown [5,6] that boron is responsible for the semiconducting properties of p-type natural diamond (type II-B). Consequently, it is very desirable to use boron as a test case for achievement of implantation doping of insulating natural diamonds (type II-A). A number of groups have attempted to achieve p-type doping in natural diamonds by ion implantation of boron at room temperature [1,2] as well as at high temperatures [2] (1200 °C), followed by annealing up to 1400 °C. It was observed that although high temperature implantation allowed higher doses of boron to be implanted with relatively less damage to the diamond lattice, it did not lead to higher fractions of dopant atoms in electrically active sites. This could result from the compensation by vacancy clusters in the lattice left in the aftermath of the implantation and annealing cycle. Once formed, these vacancy clusters are very difficult to eliminate.

Studies on carbon ion implantation into diamond have indicated that the radiation damage introduced during implantation shows characteristics which are strongly dependent on the sample temperature during the implantation [7,8]. It was suggested that this is caused by the non-diffusability of point defects created in the collision cascades at low temperatures (for example liquid nitrogen temperature), whereas at room and higher temperatures, at least some of the interstitial atoms diffuse out of the implanted layer leaving behind an excess of vacancies. This suggests the possibility of using low temperature implantation to enhance the probability of interstitial dopants occupying vacant lattice sites during the annealing subsequent to implantation, as suggested by Prins [9]. In addition to this, some of the 'frozen in' boron projectiles resulting from the previous boron cascades spontaneously combine with vacancies in the later collision cascades. In the present experiment, through the use of carbon implantation at 77 K we have injected vacancies at a range which overlaps subsequent boron implantation at 77 K, thereby enhancing the boron substitutionality.

#### EXPERIMENTAL

We have implanted insulating natural diamonds ( type II-A ) with carbon atoms with and without subsequent boron implantation at liquid nitrogen temperature. Type II-A diamonds of dimensions  $3 \times 3 \times 0.25$  mm were cleaned in hot chromic acid prior to implantation. After implantation some of the diamonds were subjected to isochronal annealing in vacuum ( $5 \times 10^{-6}$  Torr) in the temperature range of 300 to 900 °C and others were subjected to rapid thermal anneal at 1100 °C for 2 minutes. The implantation energies were selected so as to match the range of boron ions to that of the vacancy distribution produced by the previous carbon implantation. This was achieved with the help of computer simulations using the TRIM-88 program [10]. The probability of boron atoms occupying vacant sites in the lattice is expected to be enhanced during irradiation and post implant annealing if most of the boron atoms are in the vacancy-rich region. This argument is not applicable in the case when only boron is implanted. The various implantations into type II-A diamonds are summarized in table I.

TABLE I

SAMPLE	IMPLANTED ION	ENERGY (keV)	DOSE (atoms/cm <sup>2</sup> )
1	C	200	$2 \times 10^{15}$
2	C	200	$2 \times 10^{15}$
followed by	B	120	$1 \times 10^{14}$
3	C	200	$3 \times 10^{15}$
followed by	B	120	$1 \times 10^{15}$
4	C	200	$2 \times 10^{15}$
followed by	B	120	$3 \times 10^{14}$
5	C	200	$3 \times 10^{14}$
followed by	B	120	$1 \times 10^{15}$

All the implantations were done at liquid nitrogen temperature, and the samples 3 and 5 were then brought to room temperature gradually. The samples 1, 2 and 4 were rapidly brought to 1100 °C from liquid nitrogen temperature.

All the optical measurements were performed at room temperature in the transmission mode. Photoconductivity measurements were done on samples 3 and 5 at room temperature using a Xenon lamp and a monochromator to scan the wavelength region between 350 nm to 700 nm.

## RESULTS AND DISCUSSION

The optical absorption spectra of all the diamonds were measured before and after ion implantation followed by room temperature annealing, and after higher temperature annealing in some cases. The results of these measurements are shown in figures 1 and 2. Figure 1 compares the absorption spectrum of samples 1 and 2 in the UV-VIS region after RTA and furnace annealing. It shows the radiation damage induced absorption band (GR1) [5,11] after implantation. The gradual annealing of the radiation damage has been observed to appear as a decrease in absorption of the GR1 band and a more dramatic upward movement of the absorption edge at 220 nm [12]. The samples implanted with boron have higher transmission near the absorption edge which could result from compensation of GR1 defect centers by acceptor levels induced by substitutional boron. This behaviour has been observed in natural p-type diamonds containing substitutional boron atoms [13].

The absorption spectra for sample 4 at different stages of annealing in the far infrared region is shown in figure 2. The large absorption band around  $2200\text{ cm}^{-1}$  is due to two phonon absorption by carbon atoms in the diamond lattice [14] and is present in all diamonds. The most intriguing feature of the spectra appeared at  $1064\text{ cm}^{-1}$  after implantation and RTA. This absorption band was absent before implantation and is seen only when implantation was followed by RTA at  $1100^\circ\text{C}$ . It disappeared after  $980^\circ\text{C}$  annealing for 45 minutes in all the samples. This absorption was not observed when samples were gradually brought to room temperature after implantation and then annealed. We tentatively believe that the absorption band around  $1064\text{ cm}^{-1}$  is related to nitrogen similar to the bands observed in the case of type IA natural diamonds containing large amounts of nitrogen [15]. The trace amounts of nitrogen clusters present in our samples presumably dissociated during RTA.

The results of the resistance versus temperature measurements done on samples 3 and 5 are shown in figure 3. The three orders of magnitude difference in resistance between samples 3 and 5 is significant in the light of the fact that they received the same boron fluence. The higher carbon fluence in the case of sample 3 produced larger numbers of vacancies which enhanced the probability of a boron atom to go into a substitutional site during the annealing cycle. Both of the samples demonstrated low activation energies at room temperature which are thought to be caused by conduction through the variable range hopping mechanism. However, a larger activation energy (0.37 eV) characteristic of p-type conduction by boron doped natural diamonds was observed at higher temperatures. The 0.86 eV activation in the case of sample 3 is due to interplay between substitutional boron atoms and residual defects in diamond [16].

Figure 4 shows the photo-resistance of sample 5 as a function of wavelength of the incident light. The decrease in the resistance in the presence of blue to u.v. light is caused by creation of holes by ionization of GR1 defect centers in diamond [17]. The most striking feature of the measurement was the increase in the resistance of the sample to values higher than dark resistance in the presence of yellow to red light with a peak at 600 nm. This could happen due to the light induced enhancement in the hole capture cross-section of GR1 defects in diamond. After the photoconductivity measurements, the dark resistance of the sample did not go to the same value as before the experiment. The resistance did however decrease to the normal value after the sample was annealed at room temperature for a few days. Further studies to determine the mechanism causing this phenomenon are in progress. However, the absence of any measurable photoconductivity for blue

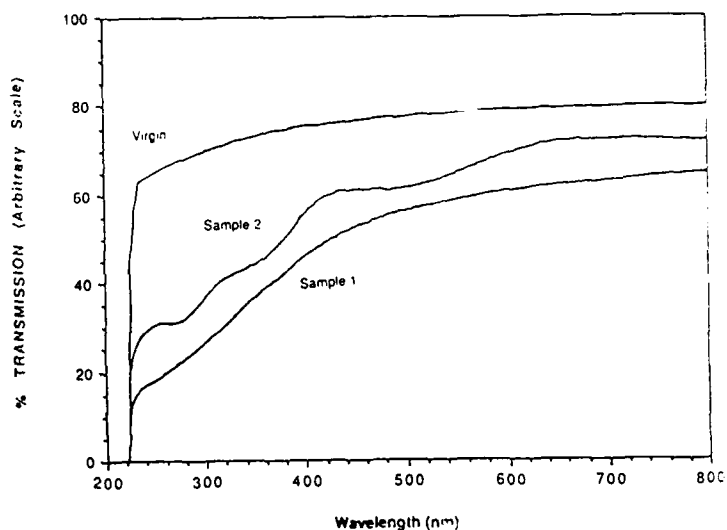


FIG. 1. U.V.-visible absorption spectra of samples 1 and 2 (see Table I) after implantations at 77K, RTA at 1100 °C and furnace annealing at 980 °C for 45 minutes. Sample 2 (implanted with boron) showed different absorption characteristics compared to sample 1 implanted with carbon only. For comparison, an absorption spectrum for an unimplanted sample is also shown.

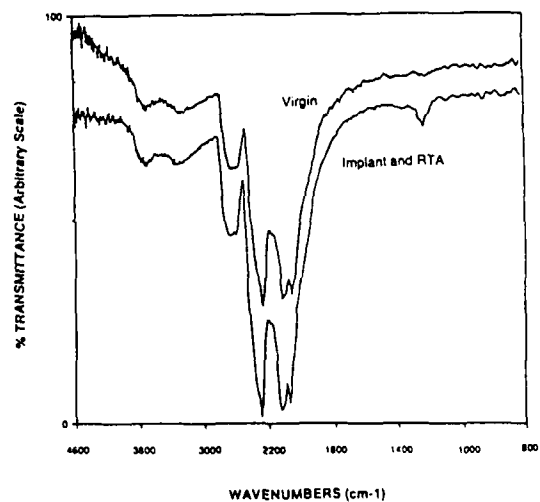


FIG. 2. I.R. absorption spectra of diamond implanted with 200 keV carbon ions and 120 keV boron ions. The sample was held at 77K during implantation and then rapidly brought to 1100 °C. The absorption peak at 1064  $\text{cm}^{-1}$  disappeared after 980 °C annealing for 45 minutes.

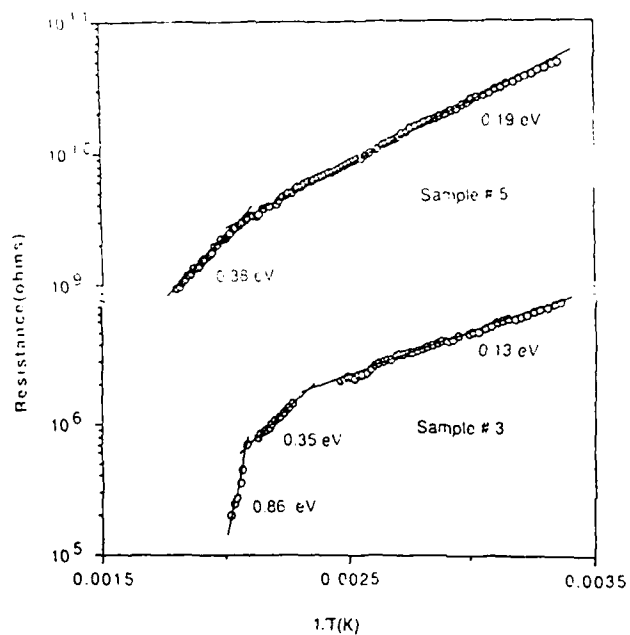


FIG. 3 Electrical resistance versus reciprocal temperature for samples 3 and 5 (see Table I) after furnace annealing and 1100°C RTA.

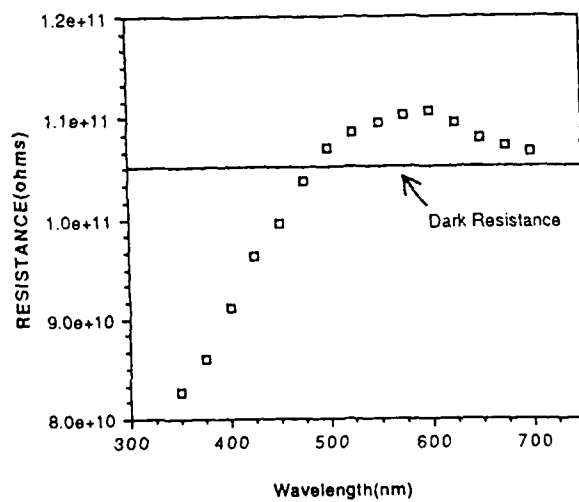


FIG. 4 Electrical resistance versus wavelength of incident light at room temperature for sample 5 after furnace annealing and 1100°C RTA.

to u.v. light in sample 3 indicates that the majority of the carriers are produced by substitutional boron acceptors and that most of the residual damage is compensated by boron acceptor centers.

#### CONCLUSIONS

We have shown that substitutional boron is produced by low temperature implantation followed by high temperature annealing. The optical absorption of implanted samples was found to strongly depend on the post implant annealing sequence as well as the relative dose of boron to carbon ions. Electrical measurements indicated the presence of substitutional boron in implanted samples. Photo-conductivity measurements indicated that the ratio of substitutional boron to residual vacancies is large and dependent on relative fluences. The number of residual vacancies in the lattice after annealing would tend to compensate p-type boron atoms and therefore would play a major role in determining the degree of success in doping of diamond. Further work to understand the results of IR absorption and photo-conductivity measurements are in progress.

#### ACKNOWLEDGEMENT

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## Appendix II

### DOPING OF DIAMOND BY ION IMPLANTATION

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#### ABSTRACT

We have implanted boron ions into insulating natural diamonds (type II-a) which were predamaged by carbon ion implantation to enhance the doping efficiency. Both implantations were performed at liquid nitrogen temperature. Samples which were subjected to rapid thermal annealing (RTA) at 1100 °C showed an optical absorption peak at 2962  $\text{cm}^{-1}$  similar to the one observed in natural semiconducting diamonds. The most intriguing feature of the spectra appeared as an absorption band around 1054  $\text{cm}^{-1}$ . The activation energies obtained from electrical measurements were found to decrease with the increasing boron fluence. We have obtained resistivities of 200  $\text{ohm-cm}$  in samples with starting theoretical resistivities of the order  $10^{17}$   $\text{ohm-cm}$ .

#### INTRODUCTION

Ion implantation is the most promising technique to dope diamonds in a controlled manner. So far, this method has yielded only limited success<sup>1,2</sup> because it requires finding annealing conditions which will drive the implanted atoms into electrically active sites and restore the diamond crystal structure, a task which is complicated by the tendency of the damaged diamond to turn into graphite<sup>3,4</sup>. When the ion dose is low enough to prevent graphitization, very few of the dopant atoms end up in electrically active sites<sup>1,4</sup>.

It has been shown<sup>5,6</sup> that boron is responsible for the semiconducting properties of p-type natural diamond (type II-B). A number of attempts to achieve p-type doping in natural diamonds by ion implantation of boron at room temperature<sup>1,2</sup> as well as at high temperatures<sup>2</sup> ( 1200 °C ), followed by annealing up to 1400 °C have met only with a limited success. It was observed that although at high temperatures one could implant higher doses of boron with relatively less damage to the diamond lattice, it did not lead to higher fractions of dopant atoms in electrically active sites. This could result from the compensation by deep electronic levels caused by residual defects in the aftermath of the implantation and annealing cycle.

It has been observed that the radiation damage introduced during carbon implantation into diamond shows characteristics which are strongly dependent on the sample temperature during the implantation<sup>7,8</sup>. It was suggested that this is caused by the non-diffusability of point defects created in the collision cascades at low temperatures (for example liquid nitrogen temperature) whereas at room and higher temperatures, at least some of the interstitial atoms diffuse out of the implanted layer leaving behind an excess of vacancies. This suggests the possibility of using low temperature implantation to enhance the probability of dopants occupying vacant lattice sites during annealing<sup>9</sup>.

TABLE I. Summary of process parameters for various Ion Implantations into diamond.  
See reference 11 for details on samples I and II.

SAMPLE	IMPLANTED ION	ENERGY (keV)	FLUENCE (atoms/cm <sup>2</sup> )
1	C	200	$2 \times 10^{15}$
2	C	200	$2 \times 10^{15}$
followed by	B	120	$1 \times 10^{14}$
3	C	200	$2 \times 10^{15}$
followed by	B	120	$3 \times 10^{14}$
4	C	200	$2 \times 10^{15}$
followed by	B	120	$6 \times 10^{14}$
I	C	200	$3 \times 10^{14}$
followed by	B	120	$1 \times 10^{15}$
II	C	200	$2 \times 10^{15}$
followed by	B	120	$1 \times 10^{15}$

#### EXPERIMENTAL

We implanted insulating natural diamonds ( type II-A ) with carbon atoms with and without subsequent boron implantation at liquid nitrogen temperature. Type II-A diamonds of dimensions 3x3x0.25 mm were cleaned in hot chromic acid prior to implantation. The implantation energies were selected so as to match the range of boron

ions to that of the vacancy distribution produced by the previous carbon implantation. The probability of boron atoms occupying vacant sites in the lattice is expected to be enhanced during irradiation and post implant annealing if most of the boron atoms are in the vacancy-rich region. This argument is not applicable in the case when only boron is implanted. The various implantations into type II-A diamonds are summarized in table I. After implantation the diamonds were subjected to rapid thermal annealing at 1100 °C for 2 minutes. The samples were kept at 77 K between the implantation and annealing steps. All the samples were then partially masked and implanted with 65 keV boron ions to  $3 \times 10^{16} / \text{cm}^2$  at room temperature in order to make ohmic contacts to the implanted layer. After optical measurements, some of the samples were furnace annealed at 980 °C for 45 minutes.

## RESULTS AND DISCUSSION

The optical absorption spectra of all the diamonds were measured before and after ion implantation followed by RTA and contact implantation. Figure 1 shows the absorption spectra for sample 4 in the far infrared region taken after implantation and RTA. The large absorption band around  $2200 \text{ cm}^{-1}$  is due to two phonon absorption by carbon atoms in the diamond lattice<sup>10</sup> and is present in all diamonds. The absorption peak at  $2962 \text{ cm}^{-1}$  is very close to the one observed to occur in natural semiconducting diamond due to substitutional boron impurities<sup>10</sup>. The most intriguing feature of the spectra appeared as a band around  $1064 \text{ cm}^{-1}$  for all three boron implanted samples with much more detailed features visible in the case of sample 4. This absorption band was absent before implantation and was seen only when implantation was followed by RTA at 1100 °C. It disappeared after 980 °C annealing for 45 minutes in the samples 2 and 3. This absorption was not observed in a similar study<sup>11</sup>, when samples were gradually brought to room temperature after implantation and then furnace annealed. One could explain the absorption band around  $1064 \text{ cm}^{-1}$  as being related to nitrogen similar to the bands observed in the case of type IA natural diamonds containing large amounts of nitrogen<sup>12</sup>. The trace amounts of nitrogen clusters present in our samples presumably dissociated during RTA. On the other hand, the obvious relationship between this band and the boron fluence tends to suggest that implanted boron atoms are somehow directly involved in producing this absorption band. There is no report in the literature about this apparently new type of absorption center in radiation damaged diamonds.

The results of the resistance versus temperature measurements done on samples 2 and 3 are shown in figure 2. Both of the samples demonstrated low activation energies

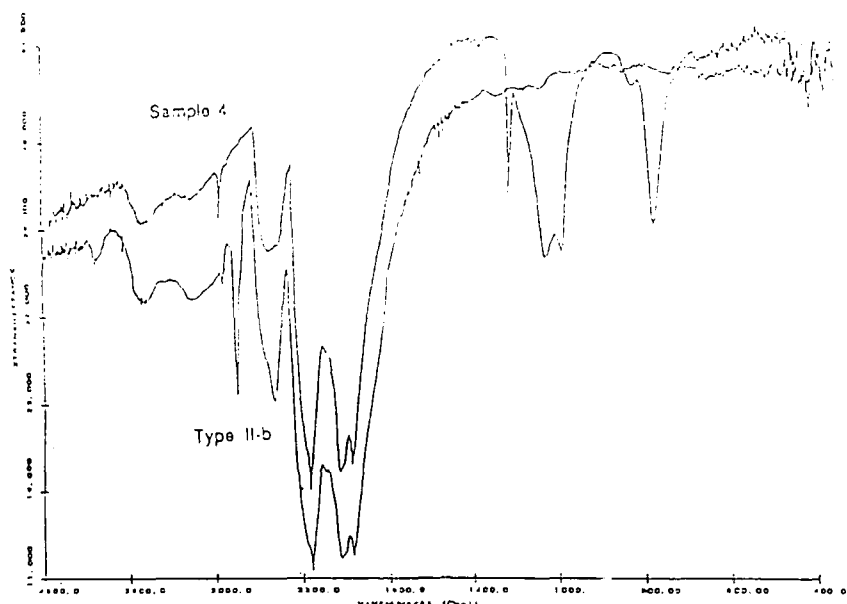


FIG.1 I.R. absorption spectra of sample 4 (see Table I) after implantation plus RTA. The sample was held at 77 K during implantation and then rapidly heated to 1100 °C. For comparison, the spectrum of type IIb diamond is also shown.

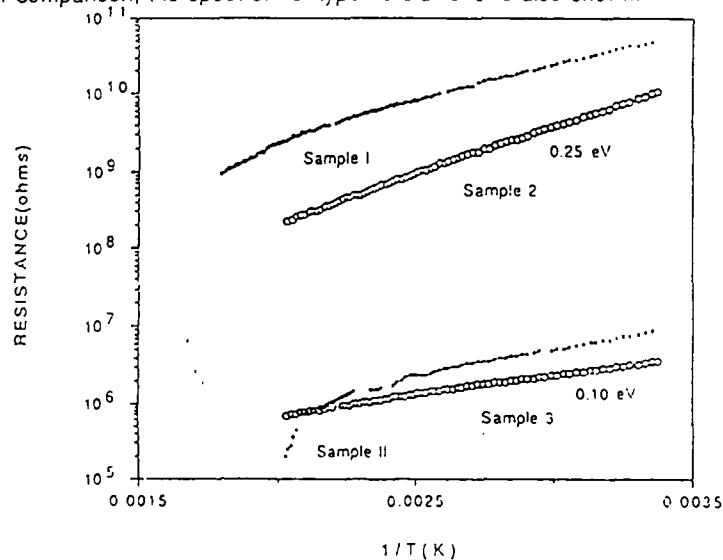


FIG.2 Electrical resistance versus reciprocal temperature for samples 2 and 3 (see Table I) after 1100 °C RTA and 580 °C annealing for 45 minutes. For comparison, the plots for samples I and II (see Table I) which were brought to room temperature after implantation and then furnace annealed upto 900 °C are also shown<sup>11</sup>

at room temperature which are attributed to conduction through variable range hopping between acceptor centers produced by substitutional boron atoms<sup>13</sup>. The resistance of the sample 1 implanted only with carbon was greater than  $2 \times 10^{13}$  ohms, which further supports our conclusion that most of the carriers were generated by substitutional boron acceptor levels. It is significant that the resistivity and activation energy of sample 3 which received a higher boron dose are lower than that of sample 2. Moreover, these samples did not demonstrate the range of activation energies seen in the case when samples were implanted under similar conditions and gradually annealed to higher temperatures (samples I and II in Table I and figure 2)<sup>9,11,14</sup>. We believe that this is due to more efficient vacancy interstitial recombination during RTA performed immediately after the 77 K implantation. During RTA, both interstitials and vacancies became mobile thus enhancing the effective cross-section for vacancy-interstitial recombination. Our recent RBS/channeling results have shown that most of the low temperature implantation damage is annealed out during RTA<sup>15</sup>. Consequently, we were able to obtain the same range of resistivities with a much lower boron fluence than in our previous experiments (samples I and II in Table I and figure 2)<sup>11</sup>.

#### CONCLUSIONS

In summary, through the use of carbon implantation at 77 K we injected vacancies at a depth which overlapped subsequent boron implantation at 77 K, thereby enhancing the boron substitutionality. Moreover, we heated the samples rapidly from 77 K to 1100 °C after implantation, thereby further increasing the probability of vacancy-interstitial recombination. Compared with the earlier furnace annealed samples, this technique produced lower resistivities and activation energies at lower boron fluences, indicating higher activation of boron atoms. Infrared absorption measurements revealed an absorption peak at  $2962 \text{ cm}^{-1}$  which is very close to the one observed in natural boron doped semiconducting diamonds ( $2930 \text{ cm}^{-1}$ ). An optical absorption band at  $1064 \text{ cm}^{-1}$  was observed after implantation and RTA which disappeared after subsequent furnace annealing. Further work to explain the data of IR absorption is in progress.

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North Carolina State University and optical measurements were performed at Research Triangle Institute (RTI) of North Carolina.

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# Doping of diamond by coimplantation of carbon and boron

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We have implanted boron ions into insulating natural diamonds which were predamaged by carbon ion implantation in order to enhance the doping efficiency. All implantations were performed at liquid-nitrogen temperature. Subsequent rapid thermal annealing at 1100 °C produced strong new optical absorption bands near 1060 cm<sup>-1</sup>, and a sharp absorption at 2962 cm<sup>-1</sup> (0.37 eV) which is close to that attributed to substitutional boron in type IIB diamond. We obtained resistivity of the order of 100 Ω cm and carrier activation energy of 0.1 eV for a sample implanted with 2 × 10<sup>15</sup> C and 3 × 10<sup>14</sup> B per cm<sup>2</sup>, indicating a high substitutional fraction of boron atoms.

It is very difficult to dope diamonds by standard diffusion techniques because of the high melting temperature of diamond. Ion implantation is the most promising technique to dope diamond in a controlled manner. So far, this method has yielded only limited success<sup>1,2</sup> because it requires finding annealing conditions which will drive the implanted atoms into electrically active sites and restore the diamond crystal structure, a task which is complicated by the tendency of the damaged diamond to turn into graphite.<sup>3,4</sup>

It has been shown<sup>5,6</sup> that boron is responsible for the semiconducting properties of *p*-type natural diamond (type IIB). A number of attempts to achieve *p*-type doping in natural diamonds by ion implantation of boron at room temperature<sup>1,2</sup> as well as at high temperatures<sup>2</sup> (1200 °C), followed by annealing up to 1400 °C have met only with a limited success. It was observed that although at high temperatures one could implant higher doses of boron with relatively less damage to the diamond lattice, this procedure did not lead to higher fractions of dopant atoms in electrically active sites. This could result from the compensation by deep electronic levels caused by residual defects in the aftermath of the implantation and annealing cycle.

It has been observed that the radiation damage introduced during carbon implantation into diamond shows characteristics which are strongly dependent on the sample temperature during the implantation.<sup>7,8</sup> It was suggested that this is caused by the nondiffusability of point defects created in the collision cascades at low temperatures (for example, liquid-nitrogen temperature) whereas at room and higher temperatures, at least some of the interstitial atoms diffuse out of the implanted layer leaving behind an excess of vacancies. This suggests the possibility of using low temperature implantation to enhance the probability of dopants occupying vacant lattice sites during annealing.<sup>9</sup> In addition to this, during the low-temperature implantation, some of the "frozen-in" boron projectiles resulting from the previous boron cascades spontaneously combine with vacancies in the later collision cascades.

We implanted insulating natural diamonds (type IIA) with carbon atoms with and without subsequent boron im-

plantation at liquid-nitrogen temperature. Type IIA diamonds of dimensions 3 × 3 × 0.25 mm were cleaned in hot chromic acid prior to implantation. The implantation energies were selected so as to match the range of boron ions to that of the vacancy distribution produced by the previous carbon implantation. The probability of boron atoms occupying vacant sites in the lattice is expected to be enhanced during irradiation and post-implant annealing if most of the boron atoms are in the vacancy-rich region. This argument is not applicable in the case when only boron is implanted. The various implantations into type IIA diamonds are summarized in Table I. After implantation the diamonds were subjected to rapid thermal annealing (RTA) in Ar at 1100 °C for 2 min. The samples were kept at 77 K between the implantation and annealing steps. All the samples were then partially masked and implanted with 65 keV boron ions to 3 × 10<sup>16</sup>/cm<sup>2</sup> at room temperature in order to make ohmic contacts<sup>10</sup> to the implanted layer. After optical measurements, the samples were furnace annealed at 980 °C for 45 min.

Figure 1 shows the absorption spectra for sample 4 in the far-infrared region taken after implantation and RTA. The large absorption band around 2200 cm<sup>-1</sup> is due to phonon absorption by carbon atoms in the diamond lattice<sup>11</sup> and is present in all diamonds. The absorption peak at 2962

TABLE I. Summary of process parameters for various ion implantations into diamond. See Ref. 12 for details on samples I and II.

Sample	Implanted ion	Energy (keV)	Fluence (10 <sup>15</sup> atoms/cm <sup>2</sup> )
1	C	200	2
2	C	200	2
followed by	B	120	0.1
3	C	200	2
followed by	B	120	0.3
4	C	200	2
followed by	B	120	0.6
5	C	200	2
followed by	B	120	1
I	C	200	3
followed by	B	120	1
II	C	200	0.3
followed by	B	120	1

<sup>a)</sup> Presently at Texas Center for Superconductivity, University of Houston, TX 77204-5506.

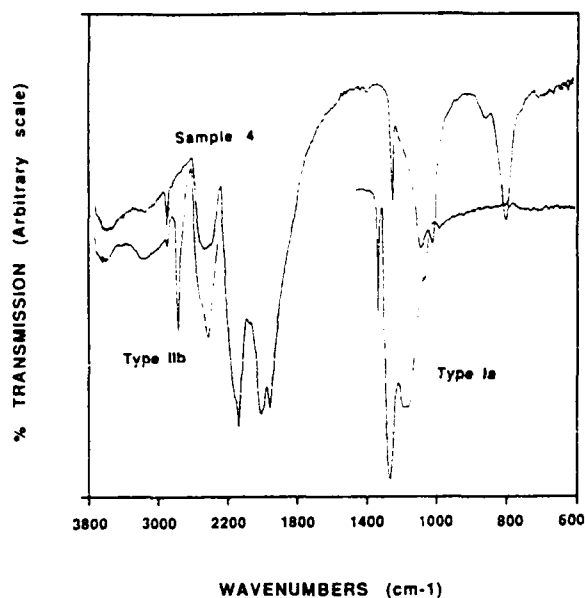


FIG. 1. IR absorption spectra of sample 4 after implantation plus RTA. The sample was held at 77 K during implantation and then rapidly heated to 1100 °C. For comparison, the spectra of type IA and IIB diamonds in the region of interest are also shown.

$\text{cm}^{-1}$  (0.37 eV) is very close to the one observed to occur in natural semiconducting diamond due to substitutional boron impurities.<sup>11</sup> The difference in absorption characteristics and a shift of 5 meV in the implanted samples could arise because of the Jahn-Teller distortions due to insufficient annealing after implantation.

The most intriguing feature of the spectra appeared from 800 to 1300  $\text{cm}^{-1}$  (largest band near 1060  $\text{cm}^{-1}$ ) and was seen only when implantation was followed by RTA at 1100 °C. This absorption was not observed in a similar study,<sup>12</sup> when samples were gradually brought to room temperature after implantation and then furnace annealed. Both the 2962 and 1060  $\text{cm}^{-1}$  absorptions increased for sample 5 (Table I) which received a higher boron fluence. One could explain the absorption band around 1060  $\text{cm}^{-1}$  as being related to nitrogen similar to the bands (also shown in Fig. 1) observed in the case of type IA natural diamonds containing large amounts of nitrogen.<sup>13</sup> On the other hand, the obvious differences in energy of the absorption bands for implanted and type IA diamond and, the observed increase in intensity of this band with boron fluence tends to suggest that the implanted boron atoms are somehow directly involved in producing this absorption band. There is no report in the literature about this apparently new type of absorption center in radiation-damaged diamonds.

The results of the resistance versus temperature measurements done on samples 2 and 3 are shown in Fig. 2. Both of the samples demonstrated low activation energies at room temperature which are attributed to conduction through variable range hopping<sup>14</sup> between acceptor centers produced by substitutional boron atoms.<sup>15-17</sup> It has been observed that for heavily doped natural,<sup>16</sup> synthetic,<sup>16,18</sup> and chemical vapor deposited<sup>19</sup> diamonds, impurity band conduction is the dominant conduction process which accounts for the wide range of activation energies seen in those experiments. The

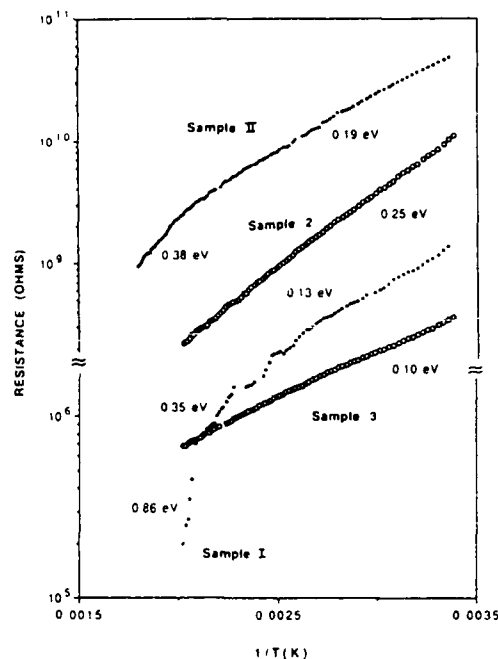


FIG. 2. Electrical resistance vs reciprocal temperature for samples 2 and 3 after 1100 °C RTA and 980 °C annealing for 45 min. For comparison, the plots for samples I and II (see Table I) which were brought to room temperature after implantation and then furnace annealed up to 900 °C are also shown.

resistance of sample 1, implanted only with carbon, was greater than  $2 \times 10^{13} \Omega$ , which further supports our conclusion that most of the carriers were generated by substitutional boron acceptor levels. It is significant that the resistivity and activation energy of sample 3 which received a higher boron dose are lower than that of sample 2. Moreover, these samples did not demonstrate the range of activation energies seen in the case when samples were implanted under similar conditions and gradually annealed to higher temperatures (samples I and II in Table I and Fig. 2).<sup>9,12,20</sup> It is noteworthy that samples I and II showed activation energies around 0.37 eV at higher temperatures which is known to be caused by the ionization of substitutional boron acceptors in diamond.<sup>16,17</sup> Therefore, unlike in the case of RTA samples, the substitutional boron atoms in the furnace-annealed samples were presumably not sitting close enough in the diamond lattice for an appreciable overlap of electron wave functions to occur. We believe that this is due to more efficient vacancy interstitial recombination during RTA performed immediately after the 77 K implantation. During RTA, both interstitials and vacancies became mobile thus enhancing the effective cross section for vacancy-interstitial recombination. Our recent Rutherford backscattering/channeling results have shown that most of the low-temperature implantation damage is annealed out during RTA.<sup>21</sup> Consequently, we were able to obtain the same range of resistivities with a much lower boron fluence than in our previous experiments (samples I and II in Table I and Fig. 2).<sup>12</sup>

Photoconductivity measurements were done at room temperature using a xenon arc lamp and a monochromator to scan the wavelength region between 300 and 700 nm. Fig-



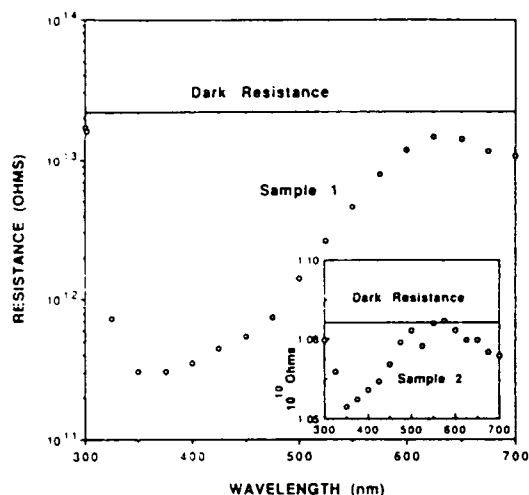


FIG. 3. Electrical resistance vs wavelength of incident light at room temperature for samples 1 and 2 (inset) after 1100 °C RTA and 980 °C annealing for 45 min.

ure 3 shows the photoresistance of samples 1 and 2 as a function of wavelength of the incident light. The decrease in the resistance of sample 1 in the presence of blue to UV light is caused by creation of holes through ionization of GR1 defect centers in diamond,<sup>22</sup> which are deep levels attributed to vacancy clusters in diamond. Sample 2 showed a much smaller change in resistance as shown in Fig. 3 (inset). However, sample 3 showed an absence of measurable photoconductivity for blue to UV light, indicating that the GR1 centers were overcompensated by the shallower boron acceptors. In general, the residual vacancies in the lattice after annealing compensate boron acceptor atoms and therefore would play a major role in determining the degree of success in doping of diamond.

In summary, through the use of carbon implantation at 77 K we injected vacancies at a depth which overlapped subsequent boron implantation at 77 K, thereby enhancing the boron substitutionality. Moreover, we heated the samples rapidly from 77 K to 1100 °C after implantation, thereby further increasing the probability of vacancy-interstitial recombination. Compared with the earlier furnace annealed samples, this technique produced lower resistivities and acti-

vation energies at lower boron fluences, indicating higher substitutionality of boron atoms. Photoconductivity measurements confirmed that a majority of the carriers were produced by substitutional boron acceptors. Optical absorption bands near 1060  $\text{cm}^{-1}$  were observed after implantation and RTA. Further work to understand the IR absorption data is in progress.

This work is supported by the Office of Naval Research contract N00014-87-K-0243. We thank J. F. Prins at University of the Witwatersrand, South Africa for useful discussions. Ion implantation was done in the microelectronics laboratory at North Carolina State University and optical measurements were performed at Research Triangle Institute (RTI) of North Carolina.

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# Reactive ion etching of diamond

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A reliable means of removing surface layers of diamond is of significant importance for microelectronics as well as for other applications such as polishing of the diamond surface. Preliminary studies using reactive ion etching with  $O_2$  and  $H_2$  showed etching rates of the order of 560 Å/min for thin carbon films and 350 Å/min for natural type II-A diamonds using 300 eV oxygen ions. Addition of a substantial percentage of Ar to oxygen in the reaction chamber did not affect the etching rate.

Since diamond is chemically inert and is the hardest material known to man, a reliable means of removing surface layers of diamond in a controlled manner is a difficult problem, but nonetheless is of significant importance for microelectronics as well as for other applications such as gem polishing. Reactive ion etching (RIE) in conjunction with photolithography might be the most suitable technique for fabrication of various device structures on diamond for microelectronics applications. Diamond-based semiconductor devices<sup>1,2</sup> may turn out to be of significant importance due to the unique physical and electrical properties of diamond. The recent success with the growth of chemical vapor deposited diamond has made it possible to consider diamond as an economically feasible material for such applications.

Ion beam assisted etching of diamond using a 2 keV  $Xe^+$  beam and a reactive gas flux of nitrogen dioxide has been reported in the literature.<sup>3</sup> The etching rate was observed to vary from 500 Å/min at 100 °C to 2000 Å/min at 0 °C. In addition, sputtering of diamond with argon and oxygen ion beams has been reported.<sup>4</sup> It was found that the sputter yield of oxygen ions varied with the incident angle of ions and that increasing the energy of oxygen ions from 0.5 to 1.0 keV did not necessarily lead to an increase in sputter yield.

We have studied the reactive ion etching with  $O_2$  and  $H_2$  for the etching of diamond surfaces. The experiments were carried out in a RIE system model 1000 TP manufactured by the Semi group. Most of the etching was performed at 200–300 W rf power with a gas flow of 40–80 cc/min and a vacuum of 65–80 mTorr inside the chamber. The dc voltage induced between the electrodes in the plasma was found to depend on the gas species inside the chamber and was generally larger for oxygen compared to hydrogen for the same process conditions. In order to make use of the more expensive diamond substrates efficiently, most of the etching was done on thin (0.25–1.0 μm) amorphous carbon films deposited on glass slides. The diamond samples were included in some of the process runs and the etching rate was found to be proportional to that for amorphous carbon films. The proportionality constant was roughly equal to the ratio of the

densities of carbon films and diamond for all the tested conditions.

The thickness of the carbon films before and after the RIE step was measured by Rutherford backscattering (RBS) analysis using a 2 MeV He ion beam. Figure 1 shows the RBS spectra for a thin carbon film on a glass substrate before and after 3 min RIE in an oxygen plasma. The signal from Si and O in the glass substrate is seen at higher backscattering energies and increased in energy as the carbon film on the top was etched. The thickness of the carbon film was computed by measuring the full width half maxima (FWHM) of the carbon peak.

We have obtained etching rates of the order of 560 Å/min for thin carbon films and 350 Å/min for natural type II-A diamonds using 0.4 keV oxygen ions at an oxygen flow of 80 cc/min and a vacuum of 65 mTorr inside the chamber. The same experimental setup was used to obtain etching rates of 300–400 Å/min for synthetic diamond samples procured from Crystallume Corp. Use of hydrogen for RIE etching gave etching rates lower than that for oxygen. Table I shows that this trend in etching rates observed in our experiment is in broad agreement with the heats of formation and reaction rates for CO, CO<sub>2</sub>, and CH<sub>4</sub> in the gas phase.

We also used argon-oxygen gas mixtures for our RIE

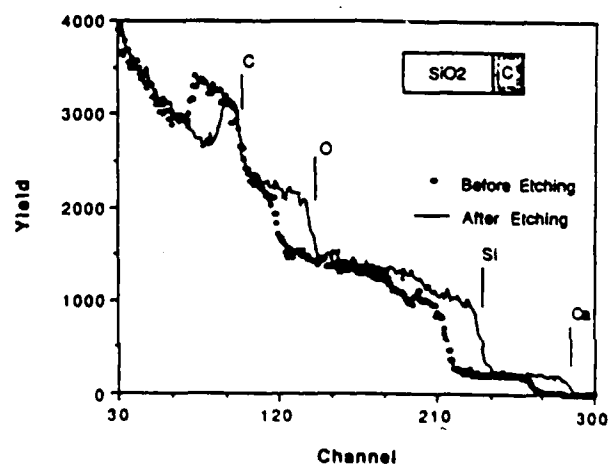


FIG. 1. RBS spectrum of thin carbon film on glass before and after etching for 3 min in oxygen plasma.

<sup>a)</sup> Presently at Texas Center for Superconductivity, University of Houston, TX 77204-5506.

TABLE I. Heats of formation and reaction rates for forming CO, CO<sub>2</sub>, and CH<sub>4</sub>. The etching rates obtained with O<sub>2</sub> and H<sub>2</sub> plasma are also shown for comparison.

Gas	WHP <sup>a</sup>	Log <sub>10</sub> Wf <sup>b</sup>	Ion energy (keV)	Etching rate (Å/min)
O <sub>2</sub>	-26.4157(CO)	24.048	0.42	500-600
	-94.052(CO <sub>2</sub> )	68.091		350-400 (diamond)
H <sub>2</sub>	-17.889(CH <sub>4</sub> )	8.899	0.38	300-330

<sup>a</sup>Standard heat of formation at 25 °C, kcal/g mole.

<sup>b</sup>Equilibrium constant for the reaction for forming given substance from its elements at 25 °C.

experiments. It was found that adding substantial amounts of Ar to the reaction chamber did not affect the etch rate. Figure 2 shows the etching rate as a function of the percentage oxygen in the gas mixture for one of the process conditions studied during this work. It shows that as we increased the percentage of oxygen from 0 to 100%, the etching rate increased rapidly at first and then saturated to a maximum of 560 Å/min. All the other process parameters were kept fixed for this set of experiments. This suggests that for a given process condition, the concentration of reactive oxy-

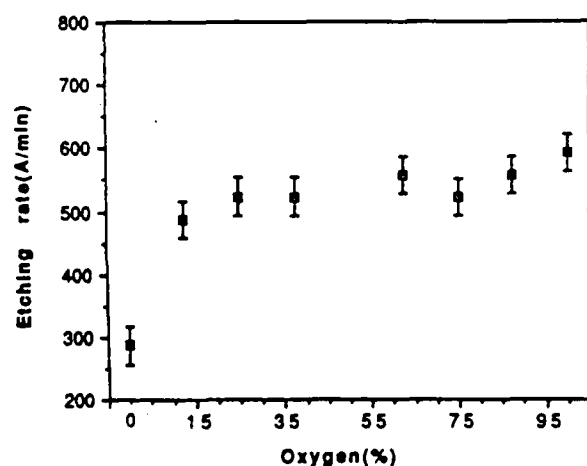


FIG. 2. Etching rate vs O<sub>2</sub>% in the Ar-O<sub>2</sub> gas mixture of carbon films for 200 W rf power with a total (Ar + O<sub>2</sub>) gas flow rate of 40 cc/min at 80 mTorr in the chamber.

gen ions available at the surface of the substrate did not depend strongly on the number of oxygen atoms in the gas mixture as long as a minimum supply of oxygen was maintained. Therefore, assuming that the etch rate depended only on the number of oxygen ions in the reaction chamber, the number of reactive oxygen ions in dynamic equilibrium with the Ar-O<sub>2</sub> gas mixture is presumably not a strong function of the partial pressure of O<sub>2</sub> in the gas mixture.

In order to increase the etching rate further, the possibility of heating the substrate and using gases like fluorine needs to be explored. The data on the reaction rate and the heat of formation of CF<sub>4</sub> suggest that the etching rate for RIE using fluorine should be higher than for the case of O<sub>2</sub>.

In summary, reactive ion etching of diamond and carbon films with oxygen, hydrogen, and argon-oxygen mixtures was studied. The maximum etching rate was obtained with oxygen and addition of a substantial percentage of argon did not have any deleterious effect on the etching rate.

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# PROCESS FOR INCREASING GOLD-DIAMOND ADHESION AND FOR IMPROVING THE SURFACE SMOOTHNESS OF GOLD FILMS ON DIAMOND<sup>1</sup>

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## I. Abstract

Integrity of adhesion of metals to diamonds which is important for heat sinks and for electrical contacts to diamonds has been a problem for years. We have solved the problem by a pre-deposition sputtering process. This process, performed at room temperature, improves the adhesions and the surface smoothness of gold films deposited on diamond. Gold films deposited by this process are not removeable by the "Scotch Tape Adhesion Test." Gold films deposited without our pre-sputtering process are affected by this test. SEM morphological studies revealed that the gold films on processed diamond have no discernible structure whereas normally sputtered films have a mosaic structure (0.1 to 1.0 micron). Ohmic gold electrodes are formed on diamond when using this process.

## II. The Process

The basics of the pre-deposition room temperature process are:

1. chemical cleaning of diamond;
2. argon sputtering of diamond for 15 minutes at  $0.2$  to  $2.0 \times 10^{-5}$  torr (argon beam 14 KeV, .25 milliamps);
3. sputtering of gold onto diamond.

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Some diamonds used in this study were contributed by the Dubbeldee Harris Diamond Corporation, D. Drukker & Zui, N. V., and the Diamond Research Laboratory of De Beers Industrial Diamond Division Ltd.

### III. Properties of the Gold Films on the Pre-deposition Sputtered Diamond

The gold films produced by this new process have both smoother surfaces and higher adhesion than similar films produced by other methods. This is evident in the structure differences between adjacent gold films prepared by this new process and by conventional methods are shown in Figure 1, and the "Scotch Tape Test" which had no effect on the gold films in pre-sputter regions of diamond but did affect gold films in the regions which were not pre-sputtered.

The gold films on semiconducting diamond were ohmic.

### IV. Conclusions

In comparison with gold films deposited on diamond by conventional methods, this new room temperature method produces gold films with:

1. higher adhesion;
2. smoother surfaces;
3. more uniform thicknesses;
4. ohmic electrode properties.

This process is expected to be applicable to other types of films on other substrates.

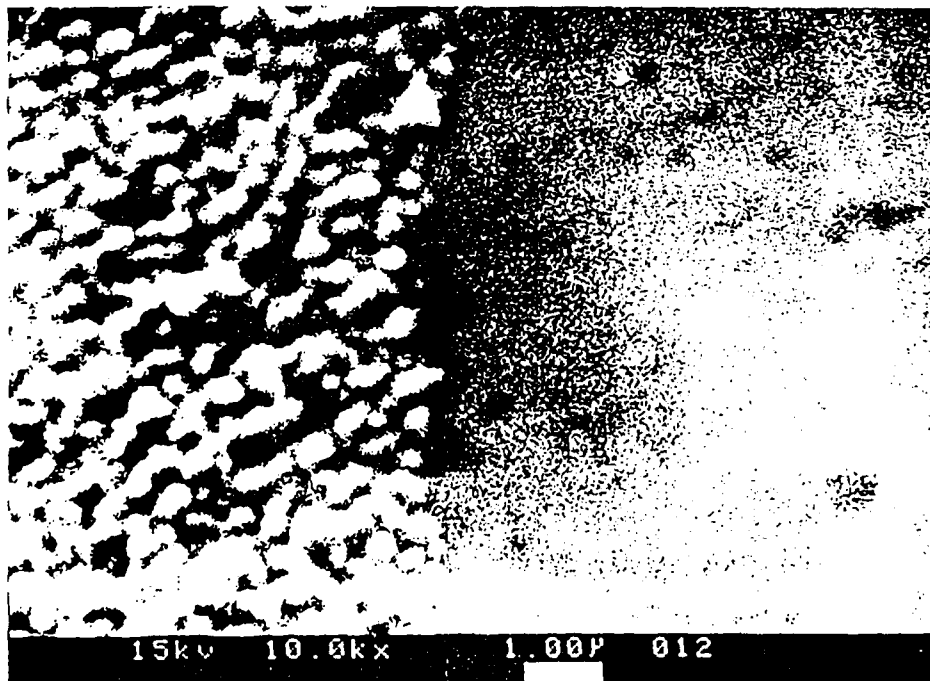


Figure 1. SEM micrograph of gold films in two different regions. The left region was not sputtered with argon prior to deposition of the gold whereas the right side was argon sputtered prior to deposition of the gold.

### Regrowth of Radiation Damaged Layers in Natural Diamond

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**Abstract.** The regrowth of radiation damaged layers created by carbon ion implantation in natural diamond was investigated by the Rutherford backscattering/channeling technique and by optical absorption. We present the first results of rapid thermal annealing of the implanted samples directly from the 77K implantation temperature to 1100°C as well as data for isochronal annealing. We found that isochronal annealing up to 900°C was more effective than rapid thermal annealing for amorphized samples. The critical dose for amorphization of diamond was between  $1.65 \times 10^{15} \text{ cm}^{-2}$  and  $3 \times 10^{15} \text{ cm}^{-2}$  for 200 keV carbon ion implantation at 77K.

## I. Introduction

Doping of diamond by means of ion implantation has been studied over the past three decades. The success of this method for the activation of dopants is limited by the difficulty in healing radiation damage created by the implantation. For example, although the damage produced by 350 keV Sb ion implantation at room temperature below a dose of  $0.9 \times 10^{14} \text{ cm}^{-2}$  can be annealed, the activation of dopant atoms is very low[1]. Above the critical dose of  $1.5 \times 10^{14} \text{ cm}^{-2}$  of 350 keV Sb ions, the large amount of radiation damage causes the diamond to graphitize upon subsequent annealing[1, 2]. Later on, hot implantations were used in an effort to reduce the radiation damage[3, 4, 5, 6]. Although graphitization can be avoided and a certain fraction of implanted dopant atoms end up on substitutional sites, the implanted layers contain a dense distribution of dislocations resulting from the agglomeration of migrating point defects[7]. These clusters of point defects, which are very stable and can not be removed even at an annealing temperature of  $1450^\circ\text{C}$ [5], tend to compensate any electrical conductivity.

Based on analysis of the previous implantation work carried out at or above room temperature on diamond, Prins[8] proposed a new approach to dope diamond by ion implantation. According to his method, diamond samples are implanted at sufficiently low temperature, e.g. liquid nitrogen temperature, by both carbon and dopant ions and annealed by rapidly heating to a high temperature directly after the implantation. Presumably this process could attain more activation of implanted dopant atoms because of the high interstitial and vacancy densities and their proximity to each other. since both vacancies and interstitials are not mobile at the implantation temperature[9]. It was unknown, however, whether the radiation damaged layers created by ion implantation could be recrystallized after the rapid thermal annealing(RTA). The critical doses of ion

implantation to create an amorphous layer, and to graphitize the diamond upon subsequent annealing were also not known. The work reported in this paper addresses this problem by investigating the regrowth of the radiation damaged layers in natural diamond produced by carbon ion implantation at 77K, using the Rutherford backscattering spectroscopy(RBS)/channeling technique and optical absorption measurements.

## II. Experimental

Four <100> orientation type Ia diamond samples were used in the present study. Some samples were reused after removal of the implanted layers by reactive ion etching using oxygen gas. All four samples had minimum yields less than 5% before implantation and thus were good single crystals.

All the samples were implanted at liquid nitrogen temperature(77K) in a nonchanneling direction with 200 keV carbon ions to doses ranging from  $10^{15}$  to  $3 \times 10^{15} \text{ cm}^{-2}$ . The dose rates were  $3.4 \times 10^{11} \text{ ions/cm}^2 \text{ s}$  for samples 1, 2, 3, and 4, and  $10 \times 10^{11} \text{ ions/cm}^2 \text{ s}$  for samples 5 and 6. Each time two samples were implanted at the same time.

Immediately after the implantations, samples 2, 4, 6 were annealed by RTA at  $1100^\circ\text{C}$  for two minutes under flowing argon in a quartz chamber. Samples 1, 3, and 5 were kept in liquid nitrogen until mounting into the target chamber for RBS/channeling analysis at 293K. Channeling measurements were done with 2 MeV He ions. The backscattered particles were analyzed with a surface barrier detector mounted at  $120^\circ$  to the incoming beam. Afterwards samples 1, 3, and 5 were isochronally annealed for one hour in a vacuum furnace with vacuum better than  $3 \times 10^{-6}$  torr. The optical



measurements in transmission mode were done on samples 2, 4, and 6 before implantations and after the implantations plus RTA's, and on samples 1, 3, and 5 before and after the implantations and after each furnace anneal, using a Perkin-Elmer Lambda 9 Spectrophotometer.

### III. Results and discussion

In Fig.1 we present the results of channeling measurements performed on samples 1 and 2 implanted with carbon ions to a dose of  $1.25 \times 10^{15} \text{ cm}^{-2}$ . The aligned spectrum of the as-implanted sample 1 (Fig.1(a)) showed a subsurface damage peak indicating a heavily damaged buried layer about 210 nm below the surface. After RTA on sample 2 at  $1100^\circ\text{C}$  for two minutes, the radiation damage was annealed. In this case we infer that the diamond structure of the damaged layers was retained after the implantation and the defects were mainly point defects and defect clusters. After heating to  $1100^\circ\text{C}$  the diamond structure did not collapse and both interstitials and vacancies were mobile and quickly recombined to heal the damage. This conclusion was supported by the optical measurements (see below). In the case of isochronal annealing, some shrinking of the damage was observed even at  $450^\circ\text{C}$ . The  $700^\circ\text{C}$  anneal almost completely annealed the radiation damage as with the RTA. It seemed that relatively few defects remained after the annealing process probably because the defect density was not high.

Fig.2 shows similar results obtained from samples 3 and 4, which were implanted with carbon ions to a dose of  $1.65 \times 10^{15} \text{ cm}^{-2}$ . The differences from samples 1 and 2 were that the damaged layer after the implantation was broader and the RBS yield almost reached the random level, and that the  $700^\circ\text{C}$  anneal left a large fraction of displaced atoms in the damaged region. At present we don't know whether the annealing

difference at 700°C was because of insufficient annealing time or because of the formation of complex defects which could only be annealed at 900°C.

From the above results we know that both  $1.25 \times 10^{15} \text{ cm}^{-2}$  and  $1.65 \times 10^{15} \text{ cm}^{-2}$  were below the critical doses for amorphization, and for graphitization upon subsequent annealing. We therefore increased the dose up to  $3 \times 10^{15} \text{ cm}^{-2}$ . Fig.3 shows the RBS/channeling spectra of samples 5 and 6. The RBS yield reached the random level and the damaged layer extended all the way to the surface after the implantation. The large near-surface damage was surprising in view of the low RBS yields just below the surface for the samples implanted at  $1.25 \times 10^{15}$  and  $1.65 \times 10^{15} \text{ cm}^{-2}$  (Figs. 1 and 2). The higher dose rate used for samples 5 and 6 could be responsible for this effect. The lower energy end of the plateau in the aligned spectrum, which corresponded to an amorphous region, showed a very broad tail (about 102 nm) indicating that the interface between the substrate and the amorphous region was not sharp. Part of the reason for this phenomenon could be due to the lowering of densities from diamond to amorphous diamond, so that the ion range became larger with increasing dose. Here we make a distinction between amorphous diamond and amorphous carbon. Amorphous diamond caused by high dose implantation still keeps a large fraction of diamond bonds and skeletal diamond structure though a large number of graphite bonds are created[10]. The mechanical properties of the amorphous diamond are essentially the same as that of diamond. Upon subsequent annealing the diamond structure may collapse to form graphite[11, 1].

After RTA at 1100°C for two minutes the RBS yield in the aligned spectrum of sample 6 was still high. This could be due to polycrystalline growth in the amorphous region due to nucleation at high temperature. The nature of this layer will be studied

further. Sample 5 was furnace annealed after the implantation and RBS/channeling analysis. After the 500°C anneal for one hour, the channeling spectrum showed a small amount of epitaxial regrowth from the crystal-amorphous interface and the amorphous region did not collapsed into graphite. But after the 900°C anneal for one hour, almost complete epitaxial regrowth occurred from the crystal-amorphous interface all the way to about 53 nm below the surface. The surface layer of about 53 nm thick became graphite, which could be easily scratched off. After being etched in chromic acid the sample was completely transparent again. We believe two processes competed during the 900°C anneal. One was epitaxial regrowth from the interface and the other was graphitization from the surface. According to Berman's line of the graphite-diamond equilibrium[12, 13], at 900°C and atmospheric pressure or below, the graphite phase is favored. That was why the surface layer of sample 5 started to graphitize during 900°C anneal. But graphitization results in volume expansion. Therefore if the deep amorphous layers graphitized, great pressure would be created, thus preventing the graphitization, if the amorphous region above were still mechanically as strong as diamond. After the interface moved near the surface to a position where there was not enough strength of the overlayer to prevent the transformation to graphite, the epitaxial regrowth stopped and the rest of the amorphous region became graphite. From this point of view, we could prevent graphitization by leaving a surface layer of about 53 nm or more unamorphized. This layer essentially acts as a blocking layer which creates pressure to prevent the transformation of the amorphous region to graphite in the annealing process. This can be achieved by deeper implantation and may give us freedom to raise the implantation dose further.

From the results obtained on samples 5 and 6 we can see that RTA at 1100°C may not be a better thermal process than isochronal annealing because nucleation in the amorphous region by RTA results in polycrystals.

Optical measurements were also employed to measure the recovery of the implantation damage. Fig.4 showed the optical spectra of sample 1 and 2 from 200 nm to 800 nm, which covers the GR1 absorption band(477~775 nm) and the u.v.-continuum(300~443 nm). Previous work has established that the GR1 band and the u.v.-continuum are caused by radiation damage in diamond[14]. The transmission spectra of the as-implanted sample 1(Fig.4(a)) showed strong absorption in the u.v.-continuum, which was the common feature observed in all the implanted samples. After RTA the absorption in the u.v.-continuum of sample 2(Fig.4(b)) was reduced substantially. This indicated annealing of the radiation damage in the sample, consistent with the result of the channeling measurement. From Fig.4(a) we can see that the absorption of sample 1 was reduced after each furnace anneal but not as much as that of sample 2. This is because the RBS analyzing beam also causes damage deep in the sample. The spot bombarded by the analyzing beam looks grey after RBS analysis and turns to brownish after RTA at 1100°C for two minutes. This residual damage also causes absorption in the u.v.-continuum. Our diamond samples were so small that we can not prevent the brownish spots in optical measurements. Therefore we do not intend to present the optical data quantitatively.

#### IV. Conclusion

We have found in this work that the critical dose of implantation for amorphizing diamond was between  $1.65 \times 10^{15} \text{ cm}^{-2}$  and  $3 \times 10^{15} \text{ cm}^{-2}$  for 200 keV carbon ions. Below this dose, the radiation damage could be annealed by either RTA at 1100°C or

isochronal annealing up to  $900^{\circ}\text{C}$ . Above this dose, RTA and isochronal annealing had very different effects. The isochronal annealing up to  $900^{\circ}\text{C}$  gave a nearly perfect crystal in the epitaxially regrown region with a graphite overlayer, whereas the RTA caused poor crystallinity, presumably because of polycrystalline growth.

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## Figure Captions

Fig. 1. RBS/channeling spectra of 200 keV carbon ion implanted diamond samples with a dose of  $1.25 \times 10^{15} \text{ cm}^{-2}$ : (a) sample 1: random(•); as-implanted(o);  $450^\circ\text{C}$ ( $\nabla$ );  $700^\circ\text{C}$ (+);  $900^\circ\text{C}$ ( $\diamond$ ); unimplanted( $\Delta$ ); (b) sample 2: random(•); RTA( $\diamond$ ); unimplanted( $\Delta$ )

Fig. 2. RBS/channeling spectra of 200 keV carbon ion implanted diamond samples with a dose of  $1.65 \times 10^{15} \text{ cm}^{-2}$ : (a) sample 3: random(•); as-implanted(o);  $450^\circ\text{C}$ ( $\nabla$ );  $700^\circ\text{C}$ (+);  $900^\circ\text{C}$ ( $\diamond$ ); unimplanted( $\Delta$ ); (b) sample 4: random(•); RTA( $\diamond$ ); unimplanted( $\Delta$ ).

Fig. 3. RBS/channeling spectra of 200 keV carbon ion implanted diamond samples with a dose of  $3 \times 10^{15} \text{ cm}^{-2}$ : (a) sample 5: random(•); as-implanted(o);  $500^\circ\text{C}$ ( $\nabla$ );  $900^\circ\text{C}$ ( $\diamond$ ); unimplanted( $\Delta$ ); (b) sample 6: random(•); RTA( $\diamond$ ); unimplanted( $\Delta$ ).

Fig. 4. Optical transmission spectra of sample 1: (a); and sample 2: (b).

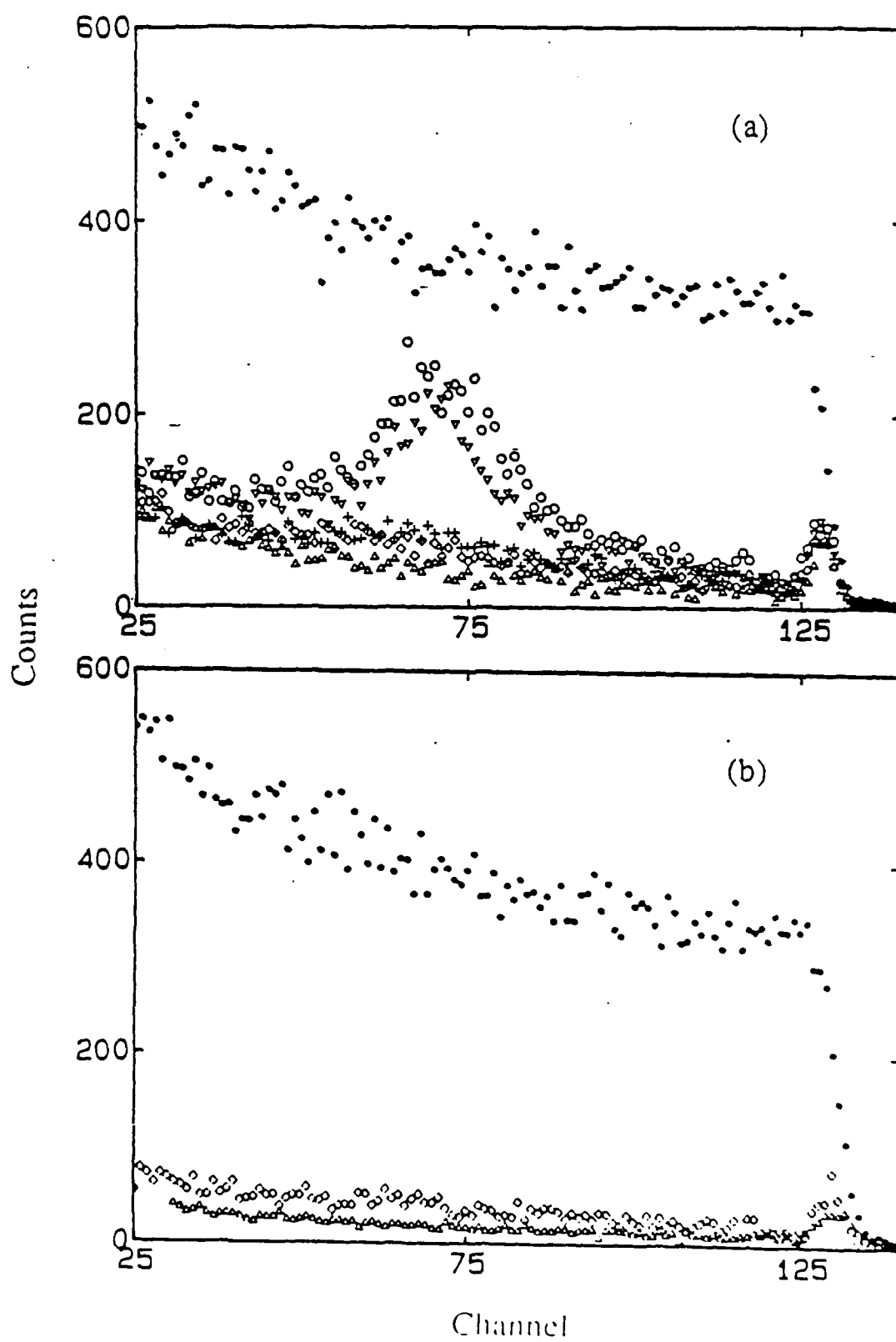




Figure 2

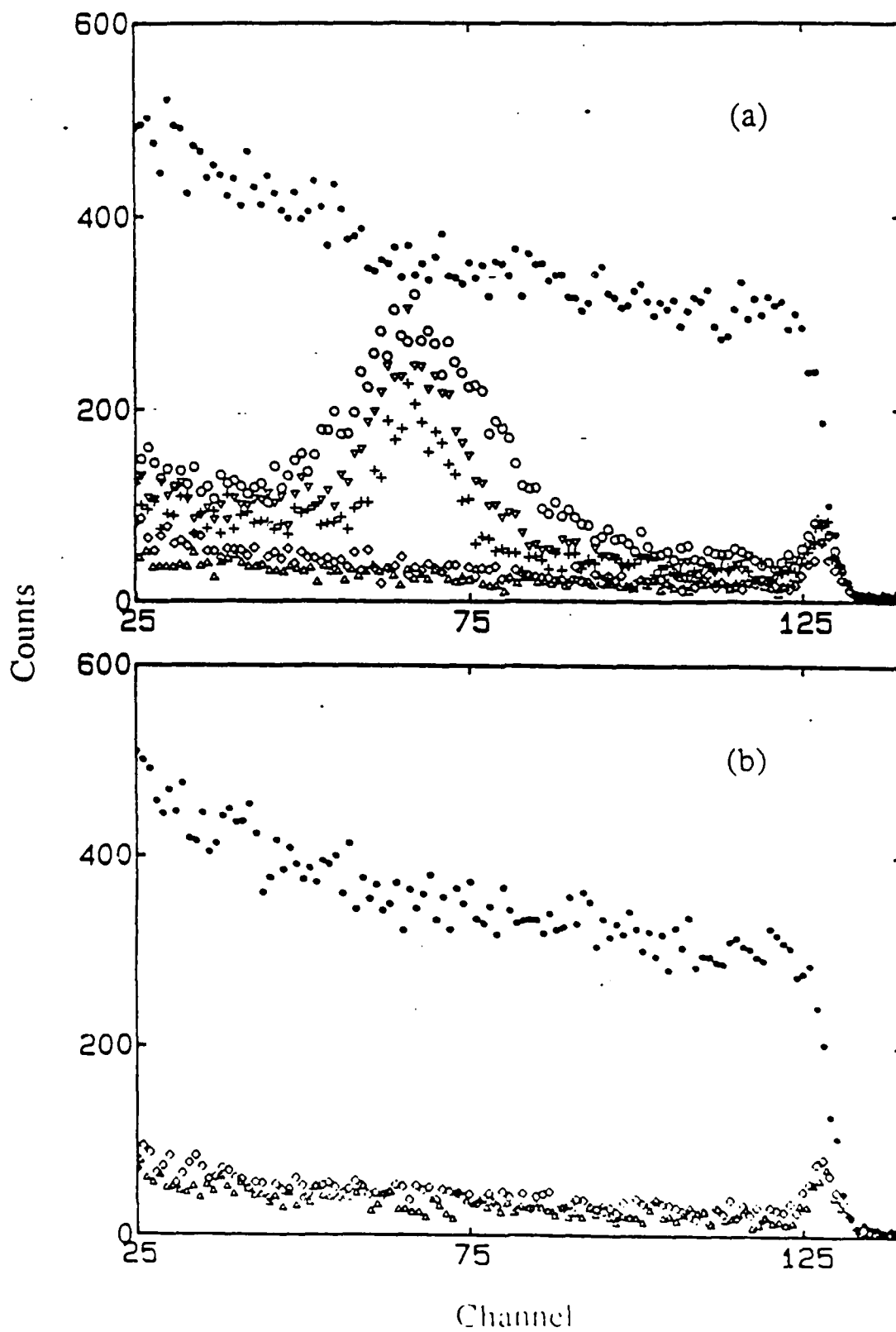


Figure 3

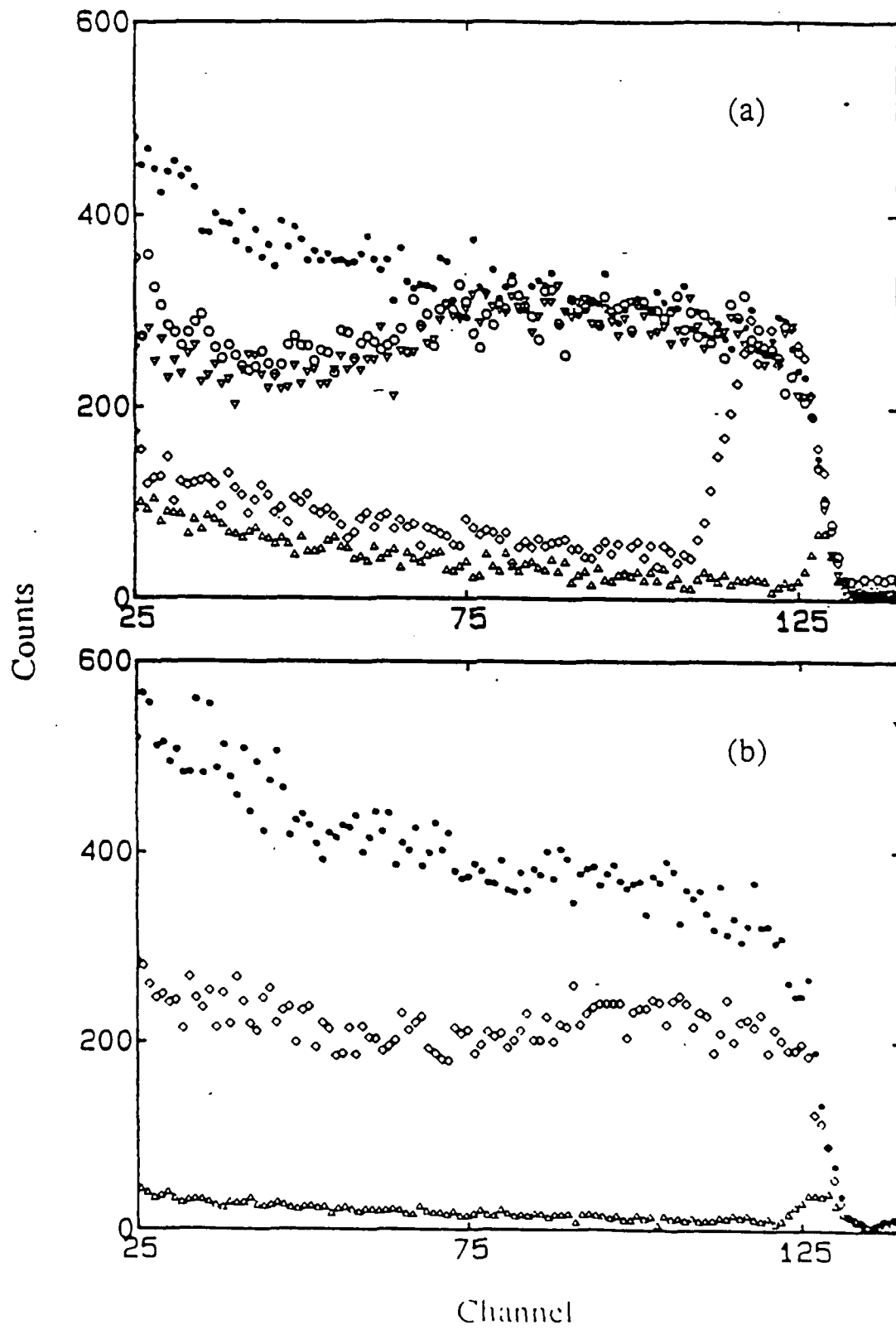
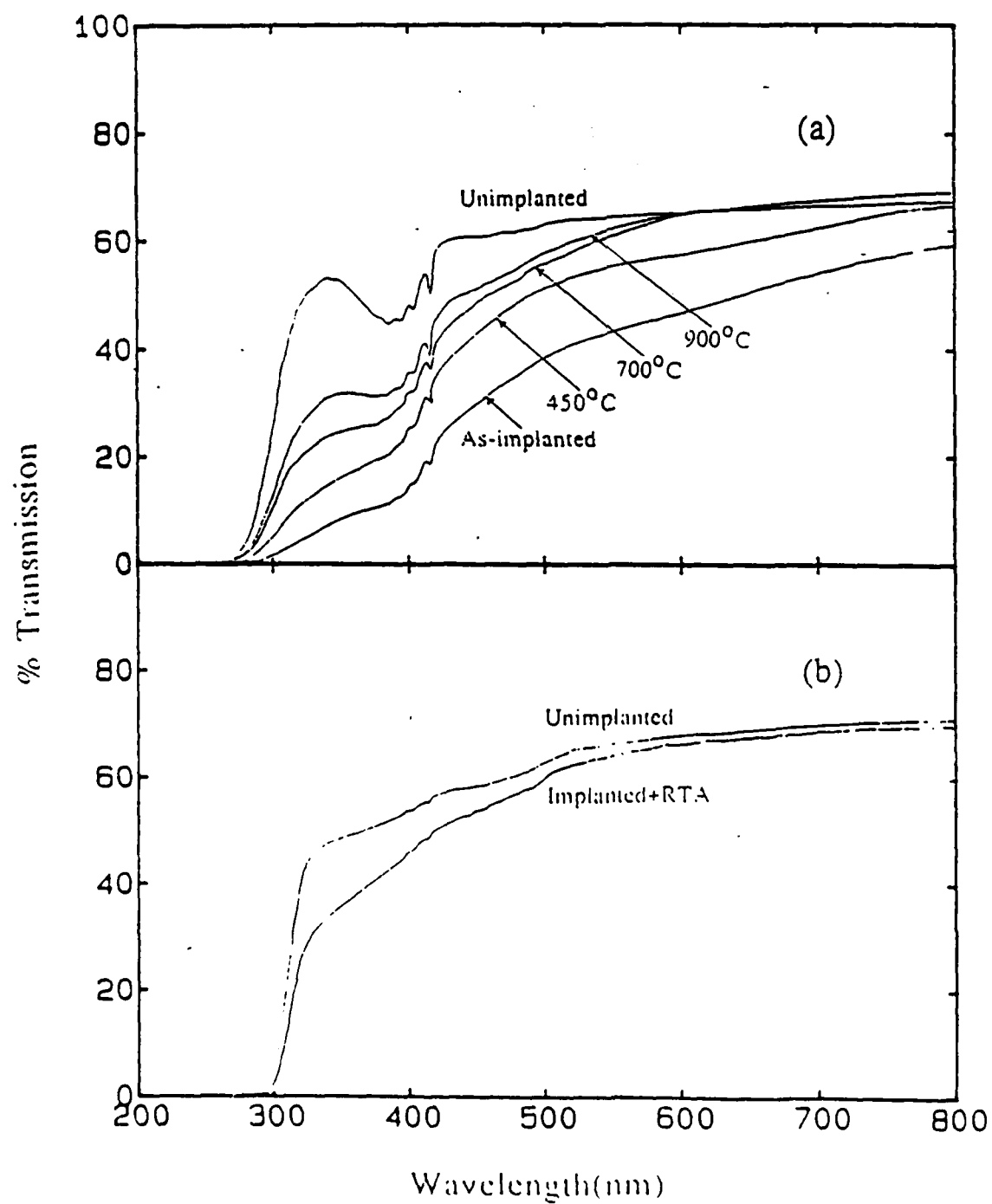


Figure 4



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Materials Processing of Diamond:  
Etching, Doping by Ion Implantation and Contact Formation

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a. Papers submitted and not yet published

"Regrowth of radiation-damage layers in natural diamond," B. Liu, G.S. Sandhu, N.R. Parikh, M.L. Swanson, W.K. Chu. To be published in Nucl. Instrum & Methods.

b. Papers published and accepted for publication

1. "Characterization of diamond-like films," W.K. Chu, G.S. Sandhu, N.R. Parikh, M.L. Swanson, C.B. Childs, J.M. Mikrut, and L.E. McNeil, SPIE Proc. 969 (1989).
2. "Doping of diamond by ion implantation," W.K. Chu, G.S. Sandhu, M.L. Swanson, SPIE Proc. 969 (1989).
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8. "Regrowth of radiation-damaged layers in natural diamond," B. Liu, G.S. Sandhu, N.R. Parikh, M.L. Swanson, W.K. Chu. To be published in Nucl. Instrum. & Methods.

c. Books submitted for publication  
none

d. Books published  
none

e. Patent filed

W.K. Chu and C.B. Childs, July 20, 1989, "Coated Substrates and Process."

f. Patents granted  
none

g. Invited presentations

"Regrowth of radiation-damaged layers in natural diamond," B. Liu, G.S. Sandhu, N.R. Parikh, M.L. Swanson, W.K. Chu. IBA Conference, Kingston, Ontario, Canada, June 1989.

"Regrowth of radiation-damaged layers in natural diamond, B. Liu, G.S. Sandhu, N.R. Parikh, M.L. Swanson, W.K. Chu. SDIO/IST-ONR Diamond Technology Initiative Symposium, Crystal City, July 11-13, 1989, Final Program Presentation and Summary.

h. Contributed presentations

"Ion Implantation of boron in diamond," G.S. Sandhu, M.L. Swanson, W.K. Chu, Materials Research Society Meeting, Boston Fall '88.

"Doping of diamond by ion implantation," G.S. Sandhu, M.L. Swanson, W.K. Chu, Materials Research Society Spring '89 Meeting, San Diego CA April 1989.

"Doping of diamond by ion implantation, G.S. Sandhu, M.L. Swanson, W.K. Chu, SDIO/IST-ONR Diamond Technology Initiative Symposium, Crystal City, July 11-13, 1989.

"Process for increasing gold-diamond adhesion and for improving the surface smoothness of gold films on diamond. C.B. Childs, G.S. Sandhu, W.K. Chu, SDIO/IST-ONR Diamond Technology Initiative Symposium, Crystal City, July 11-13, 1989.

i. Honors, awards, prizes

j. Graduate students and post-doctorals supported

Graduate students: G. Sandhu  
B. Liu